BfR

Bundesinstitut für Risikobewertung

Inter-laboratory comparison exercise on the determination of bisphenol A (BPA), bisphenol S (BPS) and aluminum (Al) from cold and/or hot water extracts of recycled paper/cardboard FCM

Part B: Determination of Al

Report on the inter-laboratory comparison exercise NRL-DE-FCM-01/2020 by the National Reference Laboratory (NRL) for Food Contact Materials

Table of contents

1 Summary

The inter-laboratory comparison (ILC) exercise NRL-DE-FCM-01/2020 (part B) was organized by the German National Reference Laboratory for Food Contact Materials (NRL-FCM) established within the Unit Product Analytics of the Department of Chemicals and Product Safety at the German Federal Institute for Risk Assessment (BfR). The ILC aimed at assessing the analytical capabilities of official control laboratories (OCLs) and NRLs in the determination of aluminum (Al) from cold water extracts (CWEs) of recycled cardboard FCM at concentrations lower than 1 mg L^{-1}. The determination of Al was optional; hence, not all laboratories submitted results. This part of the report (B) discusses only the determination of Al. Results for the determination of bisphenol A (BPA) and bisphenol S (BPS) are discussed in part A.

In 2019 BfR has introduced limits for the migration of various substances from paper or cardboard which are intended to be used in food contact at temperatures up to 90 °C (Recommendation XXXVI) [1]. According to this recommendation, the migration of Al into foodstuffs must not exceed 1 mg kg^{-1}. If tested in the CWE, a limit of 2 mg L^{-1} applies until December 31, 2020. A limit of 1 mg L^{-1} applies afterwards. Therefore, a major aspect of this ILC was to assess the analytical capabilities of the participating laboratories, especially of the OCLs, to quantify Al from CWEs at concentrations below the newly recommended limit value for the migration into food.

The participating laboratories were asked to carry out CWEs according to DIN EN 645:1994 [2]. Together with the extracts, one additionally provided solution had to be analyzed for Al.

In total, seventeen laboratories from eight EU Member States took part in this ILC, sixteen laboratories reported results for Al.

For the determination of Al each participant received one sample and one already prepared extract solution (acidified mixture of CWEs). The homogeneity and stability of all test items were evaluated beforehand by the German NRL-FCM.

The assigned values for Al and its standard uncertainties were determined by the German NRL-FCM within a homogeneity study.

The evaluation of the ILC was done on the basis of z and ζ scores in accordance with ISO 13528:2015 [3]. Based on the modified Horwitz equation [4, 5] and an expert judgment, relative standard deviations for proficiency assessment (σ_{pt}) were set to 22 % of the assigned values for extracts and to 15 % for the solution.

Inductively coupled plasma (ICP) in combination with mass spectrometry (MS) was the mainly used analytical technique for the analysis of Al. A few laboratories used ICP coupled with optical emission spectrometry (OES). One laboratory used flame atomic adsorption spectroscopy (FAAS).

The ILC revealed that the analytical methods applied by all laboratories work very well for the analysis of Al in the provided solution. All participating laboratories received satisfying z scores.

Most of the participating laboratories (12 of 16) performed satisfactory (according to z scores) for the analysis of Al from CWE of cardboard FCM according to DIN EN 645:1994 [2] at concentrations that are significantly lower than 1 mg L^{-1} (limit in Recommendation XXXVI of BfR [1]). Three laboratories out of sixteen received questionable z scores and only one achieved an unacceptable z score.

The majority of the laboratories (13 of 16) obtained acceptable ζ scores for analysis of Al in the provided solution. However, only 31 % of the laboratories (5 of 16) obtained acceptable ζ scores for the analysis of Al from CWE of cardboard FCM. For three of these laboratories, underestimation of the measurement uncertainty (MU) was identified as a main reason for the

unacceptable ζ scores. For eight laboratories the unacceptable ζ scores resulted from a combination of both the underestimation of the MU and the deviation of the reported results from the assigned value.

In general, this ILC demonstrates that the determination of Al from CWEs of paper/cardboard FCM according to DIN EN 645:1994 [2] works well regarding the new limit value of 1 mg L^{-1}.

2 Introduction

The inter-laboratory comparison (ILC) exercise on the determination of bisphenol A (BPA), bisphenol S (BPS) and aluminum (Al) from cold and/or hot water extracts was organized by the German National Reference Laboratory for Food Contact Materials (NRL-FCM) established within the Unit Product Analytics of the Department of Chemicals and Product Safety at the German Federal Institute for Risk Assessment (BfR). It was mandatory to analyze BPA, whereas the analysis of BPS and Al were optional. Cold water extracts (CWEs) for the analysis of Al had to be prepared according to DIN EN 645 [2] followed by filtration (syringe filter, maximal pore size: 0.45 μm) and acidification according to DIN EN 12498 [6]. Additionally, the concentration of Al in one provided solution had to be determined.

In 2019 BfR has introduced limits for the migration of various substances from paper or cardboard which are intended to be used in food contact at temperatures up to 90 °C (Recommendation XXXVI [1]). According to this recommendation, the migration of Al into foodstuffs must not exceed 1 mg kg^{-1}. If tested in the CWE, a limit of 2 mg L^{-1} applies until December 31, 2020. A limit of 1 mg L^{-1} applies afterwards. Therefore, one of the aims of this ILC was to assess the analytical capabilities of the laboratories to quantify Al at concentrations close to and below the limit values stated in the BfR recommendation.

Each participant received:

- Sample 1: cardboard dish for cold water extract (for the determination of BPA, BPS and Al)
- Sample 2: pizza box for hot and cold water extract (for the determination of BPA and BPS)
- Sample 3: paper tissue for cold water extract (for the determination of BPA and BPS)
- Solution 1: aqueous solution for the determination of BPA and BPS
- Solution 2: aqueous solution for the determination of BPA and BPS
- Solution 3: aqueous solution for the determination of Al (in 1 % HNO$_3$)

Solution 3 was an acidified mixture of 24 CWEs from sample 1 and 2 (12 each) prepared in the labs of the German NRL-FCM. The individual extracts were used to determine the homogeneity of sample 1 beforehand.

For an additional study, the participants were asked to send aliquots (~5 ml) of the respective extracts to the German NRL-FCM. These solutions were subsequently analyzed on a single analytical instrument in order to compare the extracts without the influence of laboratory bias and differences in measurement precision.

This proficiency test was open to official control laboratories (OCL) and NRLs. The sixteen laboratories listed here are kindly acknowledged for their participation in the ILC exercise. The laboratory codes were allocated randomly to the participants and do not correspond to the alphabetical order shown here.

Table 1: List of participants

Organization	Country
Bayerisches Landesamt für Gesundheit und Lebensmittelsicherheit (LGL) (OCL)	Germany
Bundesinstitut für Risikobewertung (BfR) (NRL)	Germany
Chemisches und Veterinäruntersuchungsamt (CVUA) Stuttgart (OCL)	Germany
Chemisches und Veterinäruntersuchungsamt Münsterland-Emscher-Lippe (CVUA-MEL) (OCL)	Germany
Escola Superior de Biotecnologia, Universidade Católica Portuguesa (NRL)	Portugal

General Chemical State Laboratory, 2nd Chemical Service of Athens Food Contact Materials Laboratory (NRL)	Greece
Health Board Central Chemistry Laboratory (NRL)	Estonia
Landesamt für Verbraucherschutz (LAV) Sachsen-Anhalt (OCL)	Germany
Landesbetrieb Hessisches Landeslabor (LHL) (OCL)	Germany
Landeslabor (LL) Schleswig-Holstein (OCL)	Germany
Landesuntersuchungsamt (LUA) Rheinland-Pfalz (OCL)	Germany
Landesuntersuchungsanstalt für das Gesundheits- und Veterinärwesen (LUA) Sachsen (OCL)	Germany
National Institute of Public Health (SZU) (NRL)	Czech Republic
National Laboratory of Health, Environment and Food (NRL)	Slovenia
The Public Analysts Laboratory Sir Patrick Dun's Hospital (NRL)	Ireland
Zentrales Institut des Sanitätsdienstes der Bundeswehr München (UA Bundeswehr) (OCL)	Germany

This report summarizes the outcome of the ILC exercise regarding the determination of Al. Results for the determination of BPA and BPS have been discussed in part A of the report.

3 Scope

As stated in Regulation (EU) 2017/625 [7] one of the core duties of NRLs is to organize ILCs and proficiency tests between OCLs. The present ILC aims to assess the analytical capabilities of NRLs and OCLs on the determination of analytes from cold and/or hot water extracts. The participants were asked to carry out cold water extracts of recycled paper/cardboard FCM. Together with the extracts, a solution provided by the German NRL-FCM had to be analyzed.

This ILC is identified as "NRL-DE-FCM-01/2020".

4   Set up of the exercise

4.1   Time frame of the ILC

The ILC NRL-DE-FCM-01/2020 was announced on January 29, 2020. Registration was open until February 21, 2020. Samples were sent to the participants on February 28, 2020 and the deadline for reporting the results was set to April 09, 2020. This deadline was extended due to COVID-19 restrictions until the end of June. The last regular results were received on May 26, 2020; two laboratories were not able to stick to the deadline at the end of June. However, one lab reported results shortly after the preliminary results were sent to the participants.

4.2   Quality assurance

The German NRL-FCM is accredited according to: ISO/IEC 17025 [8] (certificate number: D-PL-18583-02). The reported results were evaluated following the relevant administrative and logistic procedures.

4.3   Confidentality

The procedures used for the organization of this ILC guarantee that the identity of the participants and the information provided by them is treated confidentially. The participants in this ILC were assigned with a random and unique laboratory code used throughout this report.

4.4   Distribution

Each participant received:
- Sample 1: cardboard dish for cold water extract (for the determination of BPA, BPS and Al)
- Sample 2: pizza box for hot and cold water extract (for the determination of BPA and BPS)
- Sample 3: paper tissue for cold water extract (for the determination of BPA and BPS)
- Solution 1: aqueous solution for the determination of BPA and BPS
- Solution 2: aqueous solution for the determination of BPA and BPS
- Solution 3: aqueous solution for the determination of Al (in 1 % HNO_3)
- NRL_DE_FCM_01_2020_Confirmation of receipt.pdf
- NRL_DE_FCM_01_2020_Instructions.pdf
- NRL_DE_FCM_01_2020_Questionnaire_Results.xlsx

4.5   Instructions to participants

Detailed instructions to the participants were given in the "NRL_DE_FCM_01_2020_Instructions.pdf" (see 12.1 Instructions).

Participants were asked to check and report whether the test items were undamaged after transport using the "NRL_DE_FCM_01_2020_Confirmation of receipt.pdf" form.

The questionnaire form is divided into three sheets: "General", "C&HWE" (cold and hot water extracts), and "Results". The sheet "General" contains questions about the analytical methods. Detailed information about the experimental procedure was requested in the sheet "C&HWE". In the sheet "Results", the single results should be given together with the corresponding measurement uncertainty and the coverage factor.

Participants were asked to prepare cold water extracts of recycled cardboard FCM according to DIN EN 645 [2] to determine Al. Additionally, participants were asked to determine the concentration of Al in a provided solution. For a further study participants were asked to send aliquots of each of the respective extracts (~5 ml, filtrated and stabilized according to DIN EN 12498 [6]) to the German NRL-FCM.

5   Test items

5.1   Preparation

5.1.1   Recycled cardboard FCM

Commercially available cardboard dishes were cut in 1 cm^2 pieces according to DIN 645 [2], stored in a wide neck barrel and mixed by manually shaking. The samples (10 g) were prepared out of this mixture, wrapped in aluminum foil and sent to the participants. As the sample was originally dedicated for the determination of BPA/BPS only, it was decided to use aluminum foil for packaging. Our preliminary experiments demonstrated that there is no significant influence of storage in aluminum foil on the content of Al in dry samples.

5.1.2   Solutions

Solution 3 was an acidified (1 % HNO_3) mixture of 24 cold water extracts from samples 1 and 2 (12 each). The produced mixture was then homogenized by intensive shaken. Aliquots (15 ml) were filled into plastic tubes and stored at 4 °C until shipment to the participants.

5.2   Homogeneity and stability

The homogeneity of sample 1 and solution 3 was tested beforehand by the German NRL-FCM using samples from the same mixture (see 5.1.1 Recycled cardboard FCM and 5.1.2 Solutions) as was used for the ILC. The homogeneity evaluation was done according to ISO 13528:2015 [3]. Sample 1 and solution 3 were proved to be adequately homogeneous. The detailed results are shown in 12.2 Homogeneity and stability of the samples and solutions.

The stability of solution 3 was tested by the German NRL-FCM over a period of 154 days (22 weeks; from February 12, 2020 to July 14, 2020) covering the entire ILC period. The results of the stability study (according to ISO 13528:2015 [3]) confirm that solution 3 is stable over the entire period of the ILC exercise (see 12.2.3 Stability assessment for solution 3). Because Al is not volatile and its stability in solution was confirmed, sample 1 was considered to be stable by expert judgement.

6   Assigned values and standard uncertainties

The assigned values for Al and its standard uncertainty were determined by the German NRL-FCM within a homogeneity study. The values of σ_{pt} were set to 15 % for the analysis of the solution by perception of experts. The value of σ_{pt} for the determination of Al in the CWE of sample 1 was set to 22 % based on the modified Horwitz equation [4, 5] and expert judgement. The standard uncertainty of the assigned value was estimated as:

$$u(x_{pt})=1.25\frac{s^*}{\sqrt{p}}$$ Equation 1

where s^* is the robust standard deviation of mean values (according to the Q/Hampel method [3, 9]) for samples analyzed in duplicate and p is the number of analyzed samples (n = 10). Table 2 presents the relevant parameters needed for scoring.

Table 2: Assigned range related to the determination of Al in extracts and solutions.

Test	x_{pt} ± $U(x_{pt})$*		σ_{pt}		$u(x_{pt})/\sigma_{pt}$
	[mg L^{-1}]		[mg L^{-1}]	[% of x_{pt}]	
Cold water extract (CWE)					
Sample 1	0.350 ±	0.031	0.077	22	0.198
Solutions					
Solution 3	0.356 ±	0.021	0.053	15	0.197

* $U(x_{pt})$ is the expanded uncertainty at a given coverage factor (k = 2)
Since the results from LC-001 were received after the Preliminary Report was sent to the participants, these values were not included in the estimation of x_{pt}, σ_{pt}, and $u(x_{pt})$.

7   Evaluation

7.1   Scores and evaluation criteria

The individual laboratory performance was expressed in terms of z and ζ scores according to ISO 13528:2015 [3]. The z and ζ scores for the proficiency test results x_i were calculated as follows:

$$z_i = \frac{x_i - x_{pt}}{\sigma_{pt}}$$
    Equation 2

$$\zeta_i = \frac{x_i - x_{pt}}{\sqrt{u^2(x_i) + u^2(x_{pt})}}$$
    Equation 3

where:

x_i mean value, calculated from single values reported by the participant i

x_{pt} assigned value

σ_{pt} standard deviation for proficiency test assessment

$u(x_i)$ standard uncertainty of mean value from participant i

$u(x_{pt})$ standard uncertainty of the assigned value

The interpretation of the z and ζ performance scores is done according to ISO 13528:2015 [3]:

$\|z_i\| \leq 2.00$	acceptable performance	(green in 12.3 Results of the ILC)
$2.00 < \|z_i\| < 3.00$	questionable performance	(yellow in 12.3 Results of the ILC)
$\|z_i\| \geq 3.00$	unacceptable performance	(red in 12.3 Results of the ILC)

The z score demonstrates the deviation between the participants' mean and assigned values in terms of the standard deviation for proficiency test assessment (σ_{pt}). The ζ score is a modified z score that includes uncertainties for the participants' results and the assigned value. It can be used in addition to the z score in order to evaluate whether the participants' results are close to the assigned value within their reported uncertainty.
The standard measurement uncertainty of the laboratory $u(x_i)$ was calculated by dividing the reported expanded measurement uncertainty $U(x_i)$ by the reported coverage factor k.
In order to verify how reasonable the measurement uncertainty of the laboratory is, an additional assessment was performed for each $u(x_i)$. For this reason, the relative standard uncertainty of the mean value for participant "i" was calculated:

$$u(x_i)_\% = 100\% \left(\frac{u(x_i)}{x_i} \right)$$
    Equation 4

The values of $u(x_i)_\%$ were divided into three groups:

a: $u_{min\%} \leq u(x_i)_\% \leq u_{max\%}$ reasonable estimation of $u(x_i)_\%$

b: $u(x_i)_\% < u_{min\%}$ underestimation of $u(x_i)_\%$

c: $u(x_i)_\% > u_{max\%}$ overestimation of $u(x_i)_\%$

where:

$$u_{min\%}=u(x_{pt})_{\%}=100\%\left(\frac{u(x_{pt})}{x_{pt}}\right)$$ is the minimum of the accepted relative standard uncertainty

$$u_{max\%}=\sigma_{pt\%}=100\%\left(\frac{\sigma_{pt}}{x_{pt}}\right)$$ is the maximum of the accepted relative standard uncertainty

If $u(x_i)_\%$ is in the range between a minimum and a maximum of the allowed uncertainty (case "a") the laboratory standard uncertainty may be reasonably estimated.

If $u(x_i)_\%$ is smaller than $u_{min\%} = u(x_{pt})_\%$ (case "b") the laboratory standard uncertainty may be underestimated. However, the following should be taken into account. Because the values of $u(x_{pt})$ were derived from the robust standard deviation of the single results reported by the participants, these values include contributions from (in)homogeneity, transport, and (in)stability. Therefore, a relative standard uncertainty $u(x_i)_\%$ smaller than $u(x_{pt})_\%$ is possible and plausible if these contributions are significant.

If $u(x_i)_\%$ is larger than $u_{max\%} = \sigma_{pt\%}$ (case "c") the laboratory standard uncertainty may be overestimated. However, if $u(x_i)_\% > \sigma_{pt\%}$ but x_i agrees with x_{pt} within their respective expanded measurement uncertainties, then the measurement uncertainty is properly assessed. In this case, however, the usefulness of the corresponding z score for the performance evaluation may be questionable.

7.2   General observations

Seventeen laboratories from eight EU Member States participated in this ILC. Sixteen laboratories reported results for Al.

Inductively coupled plasma (ICP) in combination with mass spectrometry (MS) was the mainly used analytical technique for the analysis of Al. A few laboratories used ICP coupled with optical emission spectrometry (OES). One laboratory used flame atomic adsorption spectroscopy (FAAS, see Table 3).

Table 3: Analytical techniques used for the determination of Al in this ILC

Technique	Al
	No. of labs
ICP-MS	11
ICP-OES	4
FAAS	1

7.3   Laboratory results and scorings

7.3.1   Performance

A graphical overview of the individual laboratory performances expressed as z and ζ scores is presented in Figure 1.
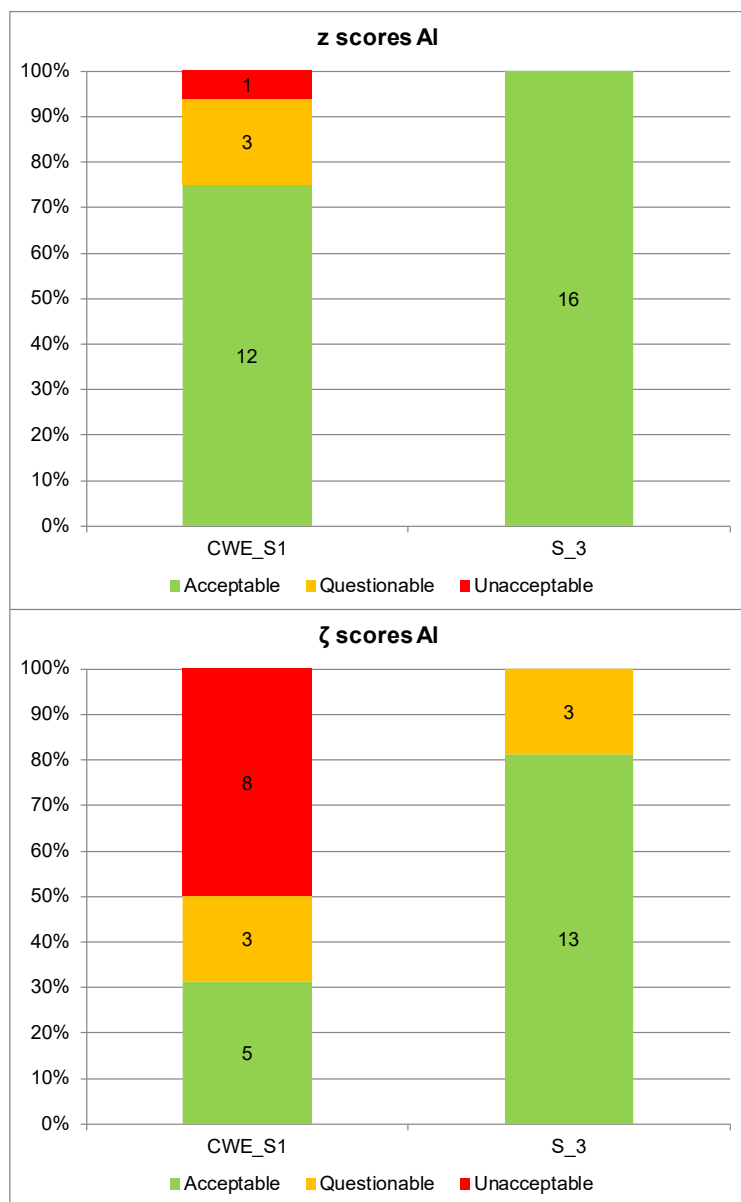
Figure 1: Overview of laboratory performances according to z and ζ scores for the analysis of Al. The numbers in the bars correspond to the number of laboratories assigned with the respective scoring. CWE_S1: cold water extract of sample 1; S_3: solution 3.

z scores
All laboratories (16 of 16) reported results with acceptable _z_ scores for the analysis of Al in solution 3.
The analysis of Al from cold water extracts of cardboard FCM according to DIN EN 645:1994 [2] at concentrations that are significantly lower than 1 mg L^{-1} (limit value in BfR Recommendation XXXVI [1]) was performed satisfactory by 75 % (12 of 16) of participating laboratories. Three laboratories reported results leading to the assignment of questionable _z_ scores and only one laboratory obtained an unacceptable _z_ score.

ζ scores
The majority of the participating laboratories (81 %; 13 of 16) received acceptable ζ scores for the analysis of Al in the provided solution. However, only 31 % of the laboratories (5 of 16) obtained acceptable ζ scores for the analysis of Al in CWEs of cardboard FCM.

For three of these laboratories, underestimation of the measurement uncertainty (MU) was identified as a main reason for the assignment of unacceptable ζ scores. For eight laboratories the unacceptable ζ scores resulted from a combination of both the underestimation of the MU and the deviation of reported results from the assigned value.
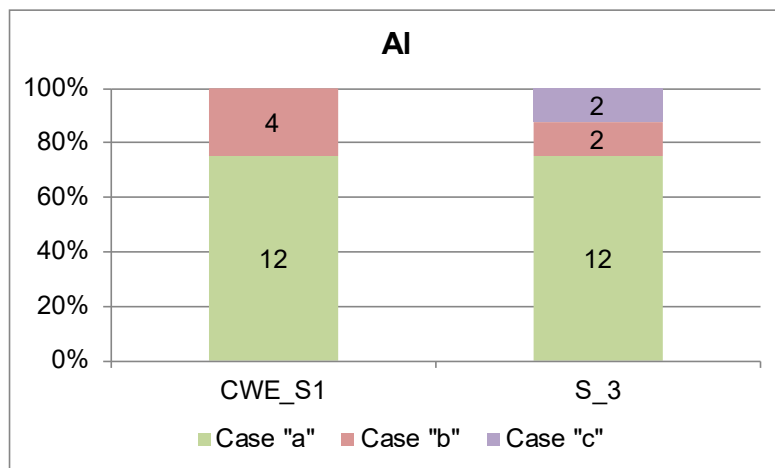
7.3.2   Measurement uncertainties (MU)

According to the questionnaire, the majority of the participants (14 from 16) provide uncertainty statements to their customers. In this ILC, all participants reported MUs for the analysis of Al. Most laboratories reported the comparable relative MUs ($U(x_i)_\%$) for the extraction experiments and for the analysis of the provided solution (see Table 4). Actually, due to the additional uncertainty resulting from the extraction process, the relative MU for an extraction experiment should be higher than that for the analysis of a solution only.

Table 4: Calculated relative MUs: $U(x_i)_\% = 100\% \left(\frac{u(x_i)}{x_i}\right)$. The values of $U(x_i)_\%$ are rounded to the nearest integer.

	$U(x_i)_\%$	
	Al	
Lab. code	CWE_S1	Sol. 3
LC-001	13	13
LC-003	14	14
LC-004	37	37
LC-005	4	3
LC-006	32	32
LC-007	10	10
LC-009	20	20
LC-010	18	20
LC-012	15	10
LC-013	14	14
LC-014	13	13
LC-015	5	4
LC-016	16	16
LC-017	25	25
LC-018	8	17
LC-019	16	7

Figure 2 depicts the evaluation of the reported measurement uncertainties for each experiment and laboratory. A detailed description of the evaluation criteria (case "a", "b" and "c") is given in section 7.1 Scores and evaluation criteria. In general, for the analysis of Al in both the extract and the solution, the estimation of the MUs was performed satisfactorily by most laboratories. For these experiments the amount of reasonably estimated MUs was higher than 75 %.

Figure 2: Evaluation of the reported measurement uncertainties for the analysis of Al. The numbers in the bars correspond to the number of laboratories assigned with the respective evaluation criteria.

Case "a": $u_{min\,\%} \leq u(x_i)_\% \leq u_{max\,\%}$

Case "b": $u(x_i)_\% < u_{min\,\%}$

Case "c": $u(x_i)_\% > u_{max\,\%}$

CWE_S1: cold water extract of sample 1; S_3: solution 3

7.4   Additional information extracted from the questionnaire

The following information was extracted from the questionnaire. All questions and answers are listed in 12.4 Results of the questionnaire. Some participants have not answered all the questions. In such cases they were not taken into account and therefore the total number of entries can differ from the total number of participants in this ILC.

General
All participated laboratories have a quality management system according to ISO 17025 [8]. Ten of fifteen laboratories used accredited methods for the analysis of Al and one laboratory a validated method; five laboratories neither validated nor accredited their methods.

Three laboratories reported that they never used this method. However, it is used for more than 5 years in 50 % of the laboratories (8 of 16). Nevertheless, this method is not frequently performed in all of the participating laboratories; only 42 % (6 of 14) of the participants use it more than fifty times per year.
Twelve out of fifteen laboratories (80 %) reported that they use certified reference materials for quality control.

Measurement uncertainty
A majority of the participants (14 from 16) reported that they provide uncertainty statements to their customers. The estimation of the measurement uncertainty is performed by an in-house validation (7 of 16), GUM ([10]; 2 of 16), Nordtest ([11]; 2 of 16); four laboratories use other estimation models.

Half (8 of 16) of the participants did not include the extraction step in the estimation of the MU. However, this may result in a significant underestimation of the MU for extraction experiments.

Blanks
Most participants (15 of 16) measured blanks, nine of them reported results after subtraction of blank values (9 of 16).

Filtration

According to DIN 645:1993 [2], the extract should be decanted or, if required, filtered. Decanting works well for paper/cardboard FCM of low swellability. However, FCM of high swellability can absorb a significant portion of the extract, preventing the efficient separation of the extract solution from the sample. The filtration of such extracts is essential. Therefore, it was specified in the instructions that extracts should be filtered.

Glass-fiber filters (size C) were used by eight laboratories for the filtration of the cold water extracts, while three laboratories used glass-fiber filters with other sizes. Three laboratories used glass frits, one laboratory used folded cellulose filters, and two laboratories did not specify their filtration equipment.

Rinsing and fill up of the volumetric flask

According to DIN 645:1993 [2], the sample should be rinsed (two times) after the filtration and the volumetric flask should be filled up to the mark. Eight laboratories filled the volumetric flasks with 11–50 ml water, five laboratories needed more than 50 ml and two needed only 0–10 ml to fill the volumetric flask up to the mark.

Stabilization / acidification

Fourteen laboratories acidified the solution before analyzing Al, one did not and one did not state it.

Filtration with a syringe filter

For the analysis of Al in the extract of sample 1 most of participants (12 of 15) used syringe filtration prior to acidification. The following filter materials were used: PTFE (6 laboratories), regenerated cellulose (2), Nylon (2), PET (1), and methyl cellulose (1). Three laboratories reported that they did not use any syringe filter. The absence of syringe filtration may result in the insufficient removal of Al-containing particles from the extract and, thus, in increased Al content in the solution after acidification. However, no clear correlation between the absence of the syringe filtration and increased z scores could be derived. Two of these laboratories reported results with strongly positive z scores (2.31 and 3.80), whereas one reported results with a negative z score (-1.39). The analysis of the provided solution 3, which was filtered and acidified prior to shipment, was performed satisfactorily by these laboratories (z scores of 1.43, 0.55, and 0.27).

8   Conclusion

All laboratories (16 of 16) obtained acceptable *z* scores for the determination of Al in the pro-vided solution (acidified mixture of CWEs).

Most of the participating laboratories (12 of 16) performed satisfactorily (according to *z* scores) for the analysis of Al from cold water extracts of paper/cardboard FCM according to DIN EN 645:1994 [2] at concentrations that are significantly lower than 1 mg L^{-1} (limit in BfR Recommendation XXXVI [1]). Three laboratories obtained questionable *z* scores (3 of 16) and only one an unacceptable (1 of 16) *z* score.

The majority of the laboratories (13 of 16) obtained acceptable ζ scores for analysis of Al in the provided solution, but only 31 % of the laboratories (5 of 16) received acceptable ζ scores for the analysis of Al from cold water extract of cardboard FCM. For three of these laboratories, the underestimation of the MU was identified as a main reason for unacceptable ζ scores. For eight laboratories the unacceptable performance (according to ζ scores) resulted from a com-bination of both the underestimation of the MU and the deviation of the reported results from the assigned value. It has to be taken into account that some laboratories do not have either an accredited or validated method for the determination of Al from cold water extracts of pa-per/cardboard FCM according to DIN EN 645:1994 [2] so far.

Most laboratories correctly estimated the MUs for the determination of Al from CWE of pa-per/cardboard FCM (12 of 16) and for analysis of Al in the provided solution (12 of 16). Almost all laboratories reported comparable relative MUs for the extraction experiments and for the analysis of the solution (acidified mixture of CWEs). However, due to the additional uncertainty resulting from the extraction process, the relative MUs for an extraction experiment should be higher than that for the analysis of an acidified CWE solution) only.

In general, this ILC demonstrates that the determination of Al from cold water extracts of pa-per/cardboard FCM according to DIN EN 645:1994 [2] works well regarding the new limit value of 1 mg L^{-1}.

9 References

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10 List of Figures

11 List of Tables

12 Annex

12.1 Instructions

Please perform cold (DIN EN 645) and hot water extracts (DIN EN 647) as specified below. Analyze the three additionally provided solutions together with the extracts. Please determine bisphenol A (BPA) and bisphenol S (BPS) for solutions no 1 and no 2 provided in glass vials and aluminum (Al) for solution no 3 provided in the plastic tube.
Solution no 1 and no 2 are aqueous, solution no 3 is aqueous with 1 % HNO_3.

For added value of this entire study, we would appreciate if you could send us an aliquot (~15 ml) of each of the respective extracts. In consequence, we will examine all incoming solutions in one sequence with our LC-MS/MS. With a growing dataset we expect to improve the data basis for the estimation of the measurement uncertainty for the estimation of BPA and BPS from cold and hot water extracts. To perform the same for Al we would welcome ~5 ml of the cold water extracts of sample no 1 in plastic tubes (sealed with Parafilm), please filtrate (syringe filter max 0.45 µm) and stabilize the extracts beforehand (according to DIN 12498).

Before starting the experiments please read the Questionnaire carefully so that you can answer all questions.

1. **Cold water extract of the commercial cardboard sample no 1 (cardboard dish) and no 2 (pizza box) according to DIN EN 645**
Please perform the cold water extracts according to DIN EN 645 in triplicate and perform a filtration, do **not** only decant the extract. We suggest using a glass-fibre filter (size C) instead of a glass frit. Please give the volume you used to wash and estimate (see questionnaire) the added volume (ml water) to finally fill the volumetric flask. Determine the BPA and BPS mass fractions in all extracts. For sample no 1 determine the Al mass fraction, additionally. Previous to the Al measurement we ask you to filtrate the extracts further by a syringe filter 0.2 µm. It is necessary to perform this filtration before stabilizing the solution (e. g. acidification according to DIN 12498).

2. **Hot water extracts of the commercial cardboard samples no 1 and 2 (cardboard dish and pizza box) according to DIN EN 647**
Please perform the hot water extracts according to DIN EN 647 in triplicate and perform a filtration, do **not** only decant the extract. We suggest using a glass-fibre filter instead of a glass frit. Please give the volume you used to wash and estimate (see questionnaire) how much ml water you had to add to finally fill the volumetric flask. Determine BPA and BPS mass fractions in the extracts.

3. **Cold water extracts of the commercial paper sample no 3 (paper tissue) according to a modified DIN EN 645 (cold water extract) method**
Please perform the cold water extracts according to DIN EN 645 in triplicate, in contrast to DIN EN 645 use only **1 g** of sample 3! Perform a filtration, do **not** only decant the extract. We suggest to use a glass-fibre filter (size C) instead of a glass frit. Please give the volume you used to wash and estimate (see questionnaire) how much ml water you had to add to finally fill the volumetric flask. Determine BPA and BPS mass fractions in the extracts and **do not** correct the value to 10 g.

12.2 Homogeneity and stability of the samples and solutions

12.2.1 Homogeneity assessment for sample 1

Table 5: Results of the homogeneity assessment of sample 1. The measurement was done in duplicate. The values are in [mg L⁻¹]. Results are evaluated according to ISO 13528:2015 (B.2.3) [3] using the expanded criterion (√c) to allow for the actual sampling error and repeatability:

	Al	
	1st	2nd
1	0.344	0.317
2	0.338	0.346
3	0.354	0.314
4	0.401	0.371
5	0.402	0.354
6	0.412	0.400
7	0.341	0.306
8	0.354	0.327
9	0.327	0.280
10	0.396	0.341
Mean	0.351	
$s_{\bar{x}}$	0.032	
s_w	0.025	
s_s	0.027	
σ_{pt} (22 % of Mean)	0.077	
σ_{allow}	0.023	
F1	1.88	
F2	1.01	
σ_{allow}^2	0.001	
c	0.002	
$\sqrt{c}$	0.041	
$s_s \leq \sqrt{c}$	passed	
Homogenous	YES	

where: $s_{\bar{x}}$ standard deviation of sample averages,

s_w within-sample standard deviation,

s_s estimate of between-sample standard deviation,

σ_{pt} standard deviation for proficiency assessment,

σ_{allow} $\sigma_{allow}=0.3\ \sigma_{pt}$; criterion of sufficient homogeneity,

F1, F2   factors for use in testing for sufficient homogeneity,

c $c=F1\sigma_{allow}^2 + F2s_w^2$; is used to expand the criterion to allow for the actual sampling error and repeatability.

12.2.2 Homogeneity assessment for solution 3

Table 6: Results of the homogeneity assessment of solution 3. The measurement was done in duplicate. The values are in [mg L^{-1}]. Results are evaluated according to ISO 13528:2015 (B.2.2) [3]:

	Al	
	1st	2nd
1	0.361	0.359
2	0.353	0.360
3	0.355	0.363
4	0.354	0.358
5	0.352	0.361
6	0.356	0.362
7	0.369	0.369
8	0.359	0.362
9	0.353	0.361
10	0.355	0.356
11	0.357	0.359
12	0.370	0.363
13	0.372	0.369
14	0.365	0.374
15	0.372	0.365
16	0.377	0.359
17	0.371	0.354
18	0.367	0.359
19	0.363	0.364
20	0.367	0.363
Mean	0.362	
$s_{\bar{x}}$	0.005	
s_w	0.005	
s_s	0.004	
σ_{pt} (15 % of Mean)	0.054	
σ_{allow}	0.016	
$s_s \leq \sigma_{allow}$	passed	
Homogenous	YES	

where: $s_{\bar{x}}$ standard deviation of sample averages,

              s_w within-sample standard deviation,

              s_s estimate of between-sample standard deviation,

              σ_{pt} standard deviation for proficiency assessment,

              σ_{allow} $\sigma_{allow}=0.3\,\sigma_{pt}$; criterion of sufficient homogeneity.

12.2.3 Stability assessment for solution 3

(Solutions were stored at 4 °C for 22 weeks)

Table 7: Results of the stability assessment of solution 3. The values are in [mg L^{-1}]. Results are evaluated according to ISO 13528:2015 (B.5.1) [3]:

Bottle ID	Al		
	#1	#2	Mean
w_0	0.339	0.347	0.34
W_{22}	0.348	0.343	0.35
$|w_0 - w_{22}|$			0.003
σ_{pt}			0.053
$0.3\ \sigma_{pt}$			0.016
$|w_0 - w_{22}| \leq 0.3\ \sigma_{pt}$			Passed
Assessment			Stable

where: w_0 results of analysis in the beginning of stability study (week 0),

w_{22} results of analysis in the end of stability study (week 22),

σ_{pt} standard deviation for proficiency assessment.

12.3 Results of the ILC

12.3.1 Results for the determination of Al in cold water extracts of sample 1
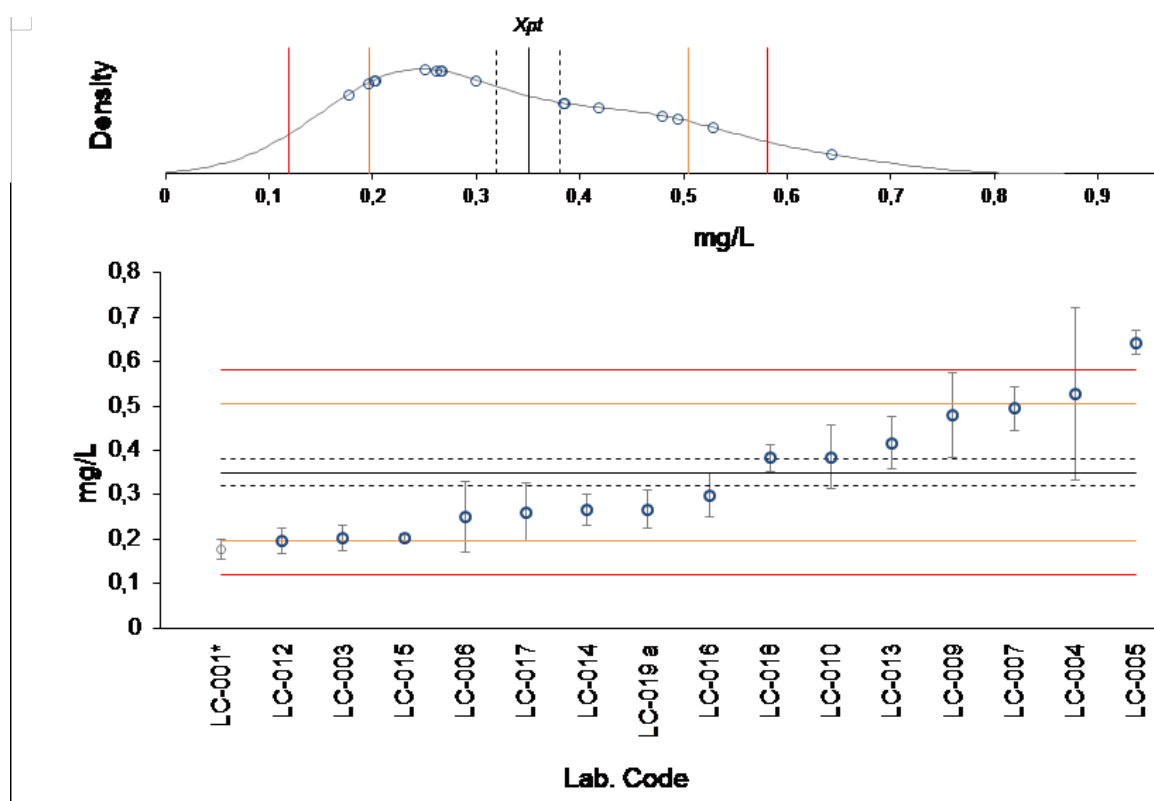
Figure 3: Measurement result range reported by the participants for the determination of Al in cold water extracts of sample 1. Circles and bars represent the reported results [x_i] with the corresponding expanded uncertainties [$U(x_i)$]; orange and red lines represent z scores = 2 and 3, respectively; solid and dotted black lines represent the assigned value [x_{pt}] and its expanded uncertainty [$U(x_{pt})$].
* The results were reported after the Preliminary Report was sent to the participants. These values were not included in the calculations of x_{pt} and σ_{pt}.

Table 8: Results for the determination of Al in cold water extracts of sample 1.
Assigned range: x_{pt} = 0.350 ± 0.031 mg L^{-1}; σ_{pt} = 0.077 mg L^{-1}; x_i and $U(x_i)$ values are in mg L^{-1}.

Lab. code	x_i	$U(x_i)$	k	z score	ζ score	$u(x_i)$ est. §
LC-001*	0.177	0.023	2	-2.25	-9.13	a
LC-003	0.201	0.028	2	-1.93	-7.15	a
LC-004	0.529	0.194	2	2.31	1.81	a
LC-005	0.643	0.028	2	3.80	14.19	b
LC-006	0.250	0.081	2	-1.30	-2.32	a
LC-007	0.494	0.049	2	1.86	4.95	a
LC-009	0.478	0.096	2	1.66	2.55	a
LC-010	0.385	0.071	2	0.45	0.90	a
LC-012	0.196	0.029	2	-2.01	-7.29	a
LC-013	0.417	0.060	2	0.87	1.98	a
LC-014	0.265	0.035	3	-1.10	-4.43	b
LC-015	0.202	0.011	2	-1.92	-9.16	b
LC-016	0.299	0.048	2	-0.66	-1.79	a
LC-017	0.261	0.065	2	-1.16	-2.47	a
LC-018	0.383	0.030	1.96	0.43	1.52	b
LC-019	0.267	0.042	2	-1.08	-3.20	a

* The results were reported after the Preliminary Report was sent to the participants. These values were not included in the calculations of x_{pt} and σ_{pt}.
§ (a) Reasonable estimation of $u(x_i)$; (b) underestimation of $u(x_i)$; (c) overestimation of $u(x_i)$.

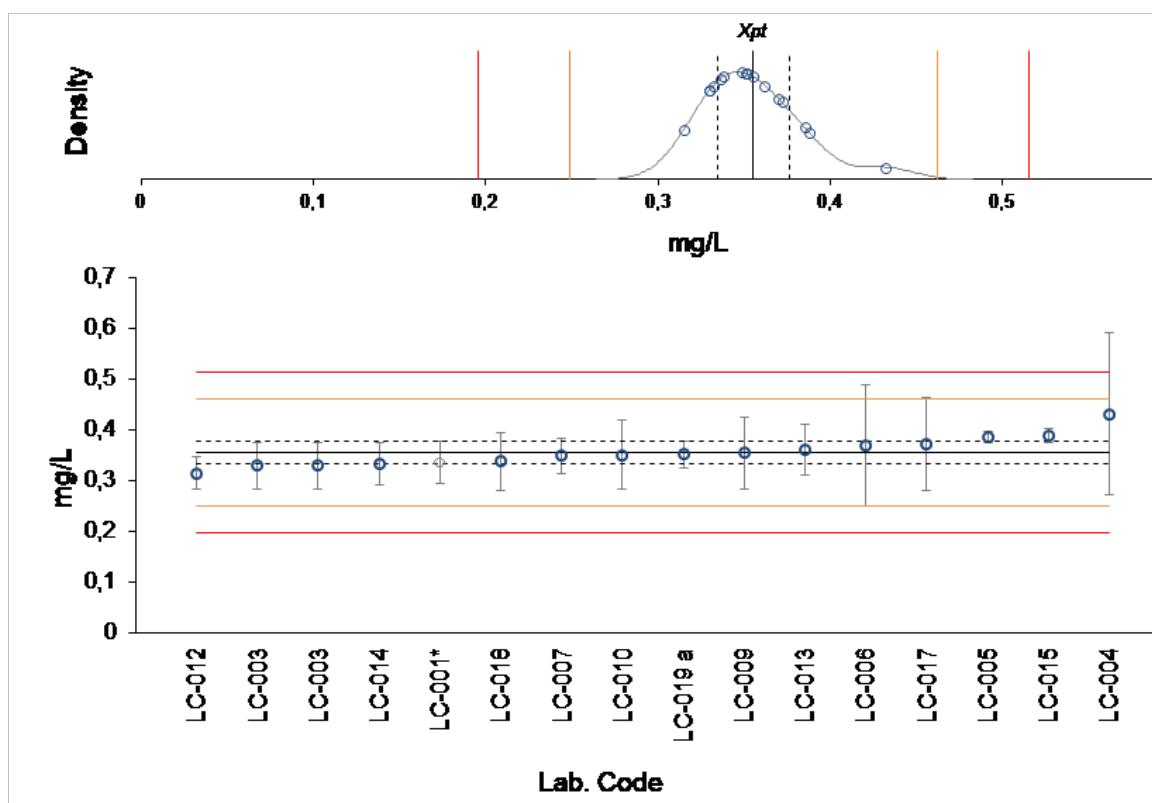## 12.3.2 Results for the determination of Al in solution 3

Figure 4: Measurement result range reported by the participants for the determination of Al in solution 3. Circles and bars represent the reported results [x_i] with the corresponding expanded uncertainties [$U(x_i)$]; orange and red lines represent z scores = 2 and 3, respectively; solid and dotted black lines represent the assigned value [x_{pt}] and its expanded uncertainty [$U(x_{pt})$].
* The results were reported after the Preliminary Report was sent to the participants. These values were not included in the calculations of x_{pt} and σ_{pt}.

Table 9: Results for the determination of Al in solution 3.
Assigned range: x_{pt} = 0.356 ± 0.021 mg L^{-1}; σ_{pt} = 0.053 mg L^{-1}; x_i and $U(x_i)$ values are in mg L^{-1}.

Lab. code	x_i	$U(x_i)$	k	z score	ζ score	$u(x_i)$ est. §
LC-001*	0.336	0.043	2	-0.37	-0.82	a
LC-003	0.330	0.046	2	-0.48	-1.01	a
LC-004	0.432	0.159	2	1.43	0.95	c
LC-005	0.385	0.011	2	0.55	2.48	b
LC-006	0.370	0.120	2	0.27	0.24	c
LC-007	0.349	0.035	2	-0.12	-0.32	a
LC-009	0.355	0.071	2	-0.01	-0.02	a
LC-010	0.351	0.069	2	-0.08	-0.13	a
LC-012	0.315	0.032	2	-0.76	-2.12	a
LC-013	0.362	0.050	2	0.12	0.24	a
LC-014	0.332	0.042	3	-0.44	-1.34	a
LC-015	0.388	0.014	2	0.61	2.57	b
LC-016	0.330	0.053	2	-0.48	-0.90	a
LC-017	0.372	0.093	2	0.31	0.35	a
LC-018	0.338	0.057	1.96	-0.33	-0.57	a
LC-019	0.352	0.026	2	-0.07	-0.23	a

* The results were reported after the Preliminary Report was sent to the participants. These values were not included in the calculations of x_{pt} and σ_{pt}.
§ (a) Reasonable estimation of $u(x_i)$; (b) underestimation of $u(x_i)$; (c) overestimation of $u(x_i)$.

12.4 Results of the questionnaire

12.4.1 General Information

Table 10: General Information

Lab code	1. Please identify yourself. You are …	2. Does your laboratory have a quality management system?	if YES, based on which standard?	3. Do you usually provide an uncertainty statement to your customer?
LC-001	NRL	Yes	ISO 17025	Yes
LC-003	NRL	Yes	ISO 17025	Yes
LC-004	NRL	Yes	ISO 17025	No
LC-005	NRL	Yes	ISO 17025	Yes
LC-006	NRL	Yes	ISO 17025	Yes
LC-007	NRL	Yes	ISO 17025	Yes
LC-009	OCL/Other	Yes	ISO 17025	Yes
LC-010	OCL/Other	Yes	ISO 17025	Yes
LC-012	OCL/Other	Yes	ISO 17025	Yes
LC-013	OCL/Other	Yes	ISO 17025	Yes
LC-014	OCL/Other	Yes	ISO 17025	Yes
LC-015	OCL/Other	Yes	ISO 17025	Yes
LC-016	OCL/Other	Yes	ISO 17025	Yes
LC-017	OCL/Other	Yes	ISO 17025	No
LC-018	OCL/Other	Yes	ISO 17025	Yes
LC-019	NRL	Yes	ISO 17025	Yes

12.4.2 Analytical method (Al)

Table 11: Information on the used analytical method (Part 1)

Lab code	1. Which analytical technique was used for the analysis of Al?	if other specify here	2. Is this method validated/accredited?	Describe shortly the way of the method validation
LC-001	ICP-MS		Accredited method	Analysis of in-house spiked materials at various concentrations and analysis of CRMs.
LC-003	ICP-MS		Validated Method	verification of linearity of calibration function, LOD, LOQ, reproducibility, repeatability, trueness, measurement uncertainty; method is validated and accredited for water matrices, not for water extracts of paper
LC-004	FAAS		Not validated/accredited	
LC-005	ICP-MS		Not validated/accredited	
LC-006	ICP-OES (axial)		Not validated/accredited	
LC-007	ICP-MS		Not validated/accredited	
LC-009	ICP-MS		Accredited method	according to VO (EG) Nr. 333/2007
LC-010	ICP-MS		Accredited method	Test method: Determination of concentrations of elements in food, consumer products, and cosmetics using the ICP-MS method (based on: L 00.00-157 (2016-03): also validated for water matrix.
LC-012	ICP-MS		Accredited method	
LC-013	ICP-OES (radial)		Accredited method	
LC-014	ICP-OES (axial)		Accredited method	The method has been validated with regard to reproducibility, accuracy, LOD and LOQ
LC-015	ICP-OES (radial)		Accredited method	
LC-016	ICP-MS	and ICP-AES	Accredited method	
LC-017	ICP-MS		Accredited method	Determination of LOD / LOQ according to DIN 32645, calculation of extended measurement uncertainty U_c from random deviation (U_{rw}) and systematic method and laboratory deviation (U_{bias})
LC-018	ICP-MS		Not validated/accredited	
LC-019	ICP-MS		Accredited method	

Table 12: Information on the used analytical method (Part 2)

Lab code	3. How long and frequently is this method used in your laboratory?		4. Do you use certified reference materials for quality control?	5. Please provide LOQs:	6. Please enter the method for the estimation of the measurement uncertainty	if other specify here	Is the uncertainty of the extraction-step included in the estimation of measurement uncertainty?
	year(s)	/year		Al [mg L-1]			
LC-001	>5	51–250	Yes	0.05	In house validation		No
LC-003	>5	1–50	Yes	0.01	In house validation		No
LC-004	2–5	1–50	No	0.009	Other	By the measurement of replicates (precision)	Yes
LC-005	<1	Never	Yes	0.004	In house validation		Yes
LC-006	<1	Never	No	0.02	Other	replicate injections of samples and standards	No
LC-007	<1	1–50	No	0.003	GUM		No
LC-009	>5	251–1000	Yes	0.002	In house validation		Yes
LC-010	>5	51–250	Yes	0.011	GUM		No
LC-012	>5	51–250	Yes	0.01	Other	T test	Yes
LC-013	>5	1–50	Please Select	0.1	In house validation		No
LC-014	>5	251–1000	Yes	0.05	In house validation		No
LC-015	1–2	Please Select	Yes	0.025	NORDTEST		No
LC-016	>5	Please Select	Yes	0.01	In house validation		Yes
LC-017	2–5	1–50	Yes	0.015	In house validation		Yes
LC-018	<1	Never	Yes	0.01475	Other		Yes
LC-019	2-5	51-250	Yes	0.007	NORDTEST		Yes

Table 13: Information on the used analytical method (Part 3)

Lab code	7. Which syringe filter did you use?	if other specify here	8. Did you test a blank sample?	if YES specify here	9. Did you subtract these blank values?	10. Did you apply any special treatment to the samples provided?	if YES specify here
LC-001	Other	methyl cellulose	No		No	Please Select	
LC-003	Other	regenerated cellulose, 0.45 µm	Yes	as blank we used deionised water, treated according to the same procedure as samples	Yes	No	
LC-004	None		Yes	Procedural blank. EN 645 without samples but with all	Yes	No	
LC-005	None		Yes		Yes	No	
LC-006	None		Yes	nitric acid 1 %	Yes	No	
LC-007	Nylon		Yes	Blank of nitric acid, with which the samples were diluted	No	Yes	dilution
LC-009	PTFE	0.45 µm	Yes	distilled water	No	No	Samples were not acidified, measured within 4 hours after extraction
LC-010	PTFE		Yes		Yes	Yes	Stabilization of extracts + blank with conc. HNO_3 (1.5 ml to 100 ml extract)
LC-012	PTFE		Yes		No	No	
LC-013	Other	PET	Yes		No	Please Select	
LC-014	PTFE		Yes		No	No	
LC-015	Please Select		Yes		No	Yes	All measurements in acetic acid 3 % and internal Standard
LC-016	PTFE		Yes	see above	Yes	No	
LC-017	Other	Regenerated cellulose	Yes	Reagent blank value and blank value carried along during sample work up	Yes	No	
LC-018	PTFE		Yes	Water as used for the water extracts without any further matrix, treated equal to the samples	Yes	No	0
LC-019	Nylon		Yes	miliq water	Yes	No	0

Table 14: Information on the used analytical method (Part 4)

Lab code	Did you encounter any problems with the sample analysis?	if YES specify here
LC-001	Yes	Due to Covid-19 difficulties and closure of the laboratory it was not possible to analyse the samples for BPS or Al within the given timeframe
LC-003	No	
LC-004	Yes	
LC-005	No	
LC-006	Yes	High measurement background
LC-007	No	
LC-009	Yes	all samples were packed in aluminium foil, although sample 1 was to be analysed for aluminium content --- could this represent a possible error source?
LC-010	Yes	
LC-012	No	
LC-013	No	
LC-014	Yes	Due to the large number of substances, co-elutions occur which can influence the response of the substances during detection and quantification.
LC-015	Yes	Solution 3 in HNO_3
LC-016	No	
LC-017	No	
LC-018	No	
LC-019	Please Select	

12.4.3 Cold water extract

Table 15: Information on the cold water extract

Lab code	1. Did you use a glass-fibre filter for the filtration of the extract-solution?	if NO specify here	2. How much water did you add to fill the volumetric flask up to the mark?	3. Did you acidify the extract solution before Al analysis?
LC-001	glass-fibre filter (size C)		more than 50 ml	Yes
LC-003	Yes, glass-fibre filter (size C)		more than 50 ml	Yes
LC-004	glass-fibre filter (size C)		11–50 ml	No
LC-005	Yes, glass-fibre filter (size C)		more than 50 ml	Yes
LC-006	Yes, glass-fibre filter (size C)		11–50 ml	Please Select
LC-007	No (Specify)	Samples were filtered through a glass frit, porosity S2 (glass-fiber filters were not available)	11–50 ml	Yes
LC-009	No (Specify)	filtration through glass frit	11–50 ml	Yes
LC-010	No (Specify)	folded filters (Sartorius; Cellulose, 185 mm; grade 1288; and before HPLC-Analysis a syringe filter PHENEX PTFE 0.45 µm)	0–10 ml	Yes
LC-012	Please Select		Please Select	Yes
LC-013	Yes, glass-fibre filter (other size)		0–10 ml	Yes
LC-014	Yes, glass-fibre filter (other size)		11–50 ml	Yes
LC-015	Yes, glass-fibre filter (size C)		11–50 ml	Yes
LC-016	Yes		11–50 ml	Yes
LC-017	Yes, glass-fibre filter (size C)		more than 50 ml	Yes
LC-018	Yes, glass-fibre filter (other size)	Glass frit as in the norm	more than 50 ml	Yes
LC-019	Yes, glass-fibre filter (size C)		11–50 ml	Yes